Characterization of Optical and Associated Properties of Marine Colored Dissolved Organic Material (CDOM)

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LONG-TERM GOALS

Our long-term goal is to understand the factors affecting the optical characteristics of seawater. Of particular interest to us are the effects of sunlight-initiated physical/chemical processes on colored dissolved organic material (CDOM), and the resultant attenuation changes in ultraviolet and visible radiation in seawater and coastal environments.

OBJECTIVES

The chemical constituent of seawater that absorbs most of the incident solar radiation is collectively referred to as CDOM. CDOM is a complex aggregate of organic compounds derived from marine biota and terrestrial humic material introduced to the oceans by rivers. The photochemically active fraction initiates most of the photochemical reactions in seawater, altering CDOM itself and affecting the chemical speciation of oxygen, transition metals and various organic compounds. These reactions can have profound effects on the chemical characteristics of seawater and physical properties such as optical absorbance and luminescence. Our primary objective is to understand the differences and similarities between DOM of marine and terrestrial origin, the effects of photochemical processes on the structure and optical characteristics of CDOM and the impact these properties have on the optical characteristics of marine environments.

APPROACH

Our approach to CDOM characterization is to use Flow Field Flow Fractionation (FFFF) as the separation technique, together with optical characterization of fractionated CDOM by in-line absorbance and fluorescence and structural characterization by LC/MS^n. Ion trap mass spectrometry (LC/MS^n) is a powerful technique for the structural characterization of complex organic molecules. This is its first application to marine CDOM. Our principal focus over the last year was to develop methods and optimize our newly purchased LC/MS^n system (funds from ONR DURIP/1999: "Application of ion trap mass spectrometry (LC/MSn) to the characterization of coastal optical properties (equipment only)" were used to purchase additional components). We used a series of riverine and marine DOM samples from South Florida waters for method development and evaluation.

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We also began photochemical studies using sunlight and UV-laser light sources to see if irradiation of fresh CDOM produces material with the same structural and optical characteristics as marine CDOM.

WORK COMPLETED

In the first year, we completed method development for the FFFF and LC/MS^n systems on schedule. s. In the second year, we completed FFFF analysis and preliminary LC/MS^n analysis on an extensive series of riverine, coastal and oceanic waters that were collected during our November, 1999 and June 2000 cruises to the west coast of Florida. The June cruise focused on CDOM, with participation from ONR-funded PI's from 5 institutions to provide a multi-faceted look at coastal processes that will be used for cooperative papers during the upcoming year. Further studies of these samples by LC/MS^n and FFFF/MS^n using laboratory photochemical techniques will continue.

1. Samples

Our primary goal is to continue to improve our knowledge on the optical and chemical properties of DOM of marine and terrestrial origin. To accomplish this a 10-day cruise on the University of Miami's R/V Calanus in November 1999 sampled river plumes on the southwest coast of Florida. The June 2000 cruise, on the new research catamaran F. G. Walton Smith, was planned to sample the Mississippi River plume in a synoptic program with the R/V Pelican, but mechanical problems delayed the Walton Smith. The cruise plan was modified to focus on fresh water CDOM sources on the south-western coast of Florida. By following a drifter placed in each river outflow, we were able to sample the same parcel of water as it aged and moved through a freshwater to marine transition zone. Samples collected represent multi-day time series for the highly tannic water of the Everglades National Park, and for the phosphate-rich, urban and agriculturally impacted waters of the Lake Okeechobee drainage. These samples were analyzed shipboard at the time of collection, as discussed below, as well as filtered and stored in the dark for further analytical work in the laboratory.

2. FFFF

Flow Field Flow Fractionation (FFFF) has been used to characterize soil and riverine humic substances (Beckett et al., 1987). Separation relies on the molecular diffusion coefficient i.e. molecular size. Eliete Zanardi, a fourth -year PhD. graduate student, whose dissertation research focuses on the FFFF analysis of marine CDOM, operated the FFFF instrumentation in near-real time aboard the Walton Smith during the June cruise providing the first ever field experimental data. In the laboratory, the FFFF system was run under a several conditions, and optimal operating parameters for DOM fractionation was determined (Zanardi et al., 2000). Molecular weight distributions were calculated from measured retention times and linear calibration curves generated with polystyrene sulfonate standards (1,800-35,000 Daltons).

3. LC/MS^n

Over the past year development of techniques to apply LC/MS^n to freshwater and marine DOM has continued. Erik Stabenau, a third year graduate student, is working with the LC/MS^n system as part of his Ph.D. research to understand the alteration of chemical features associated with changes in the optical properties of DOM in natural environments. We acquired funding (ONR Durip/1999: "Application of Ion Trap Mass Spectrometry to the Characterization of Coastal Optical Properties") to purchase a second Agilent 1100 HPLC system with fluorescence detection to enable accelerated

method development for the Ion Trap Mass Spectrometer by eliminating downtime due to switching HPLC components between the MS^n and the FFFF systems. This separate HPLC system minimizes the potential for system damage to either the LC/MS^n or the FFFF equipment due to cross-contamination of solvents, and permits stand alone operation of the FFFF on the ship. A nitrogen purification system, that eliminates our dependence on and the cost of liquid nitrogen dewers as a N_2 source, has been purchased and installed. This system allows the ion trap to be maintained in the cleanest possible manner, with high N_2 flow rates and warm temperatures, both during and between analysis to reduce system noise. Since the MS^n is to be operated as an interchangeable detector for both the FFFF and the HPLC system modifications have been made to the two computer systems that simplifies the operation of this combined system in several different arrangements including

- FFFF as a separation method with online optical detection studying diffusional related optical properties of DOM operating independent of the LC/MS^n system analyzing structural features of DOM,
- FFFF as a separation method with online optical detection followed by infusion of a eluent modifier (acetonitrile, methanol, or buffers) and detection with LC/MS^n,
- FFFF fraction collection with independent secondary HPLC separation of fractions and analysis by MS^n and,
- Uninterrupted data processing on either system while the second system continues analysis of additional samples.

RESULTS

In river water, ~98% of CDOM occurred in a 2 kDa size fraction and ~2% in a 13 kDa fraction (based on absorbance at 330 nm and fluorescence at 350/450 nm). This minor higher molecular weight fraction gradually disappeared in the river plume and was completely gone in off-shore coastal waters (Figure X). This loss may be due to dilution of the river samples and/or biological and photochemical degradation of CDOM. Irradiating a river sample with sunlight produced a fractogram characteristic of marine waters (Figure Y), suggesting that photodegradation is an important mechanism in altering the molecular and optical characteristics of CDOM.

Initial analysis using FFFF coupled with MS^n on marine and freshwater CDOM has been completed. At this point we have shown that direct ionization of CDOM without a pre-concentration step is possible by diluting the pure water mobile phase of the FFFF output with an organic modifier such as MeOH or ACN. Since no commercial library is available for the products of soft ionization of environmental macromolecules, we have begun to build this database by analysis of surrogate compounds including carboxylic acids, PAHs, and natural products (i.e. lignin).

Our novel experimental approach to DOM studies couples FFFF as the separation technique with structural characterization by LC/MS^n. Initial results of this work was presented at a national meeting in a special session on “The Origin and Reactivity of Dissolved Organic Matter”.

Clark, Catherine D., Erik R. Stabenau, Eliete Zanardi-Lamardo, Cynthia A. Moore, and Rod G. Zika (1999) "Photochemical Effects on the Structural Properties of DOM in Florida Coastal Waters: A FFFF/Ion Trap MS Study". EOS Transactions, American Geophysical Union, 80: OS145

Two papers on ONR funded research have been accepted for the Pacifichem 2000 meeting and will be presented by the graduate students who are responsible for this work.

Stabenau, E.; E. Zanardi-Lamardo, E.; C.D. Clark and R.G. Zika. "Optical Characterization of a Transect from Caloosahatchee River to Gulf of Mexico"

Zanardi-Lamardo, E.; E. Stabenau; C.D. Clark and R.G. Zika. "Photochemical Studies and Characterization of Coastal Waters in Southwest Florida"

IMPACT/APPLICATIONS

The means by which we have studied CDOM is novel and appropriate for future investigations of the structural and associated optical features of this material. Our results suggest that the photochemical degradation of terrestrial DOM from rivers forms a significant fraction of marine CDOM in coastal zones. This has significant impacts for the cycling and sources of DOM in the ocean. Correlating changes in optical characteristics with associated changes in structural features under the action of sunlight will allow us to understand how changes in ultraviolet/visible radiation occur in seawater and coastal environments. Aside from developing an understanding of the factors affecting the chemistry and physics of light in the ocean, there are other more applied potential future impacts in the development of new analytical system approaches for examining complex organic substances in the environment.

TRANSITIONS

Our results suggest that coupling FFFF as the separation technique, with structural characterization by LC/MS^n, is a promising route to elucidating the behavior of CDOM and potentially other complex organic substances in marine systems. For example, the LC/ MS^n system has been used in a study of marine coral proteins by members of the Marine Biology and Fisheries Division at RSMAS.

In general, we see a strong future for the transition of the FFFF and LC/MS^n instrumentation/ techniques to the study of other complex organic systems (eg. volatile organic carbons and polyaromatic hydrocarbons in aerosols), both in this laboratory and elsewhere.

RELATED PROJECTS

- In collaboration with Gil Jones at Boston University, we continue to examine the fluorescence lifetimes of humic materials in natural waters as a probe of the nature and distribution of the fluorophore.

- Work on developing an autonomous oceanographic monitoring system for vessels of opportunity, including superyachts and commercial cruise liners, has led to cooperation with SeaPoint Sensors,

Inc. (Rhode Island) to develop a solid state CDOM sensor. A program of deployment and comparison to traditional on-line fluorometers was partially funded by ONR.

Zika, Rod G., Catherine Clark, Geoffrey Morrison, Cynthia Moore, Tom Houston, Peter Milne (1999) "SeaKeepers Project- Progress Towards Realization of an Autonomous Oceanographic Monitoring System for Private Vessels." EOS Transactions, American Geophysical Union, 80: OS151 (Poster)

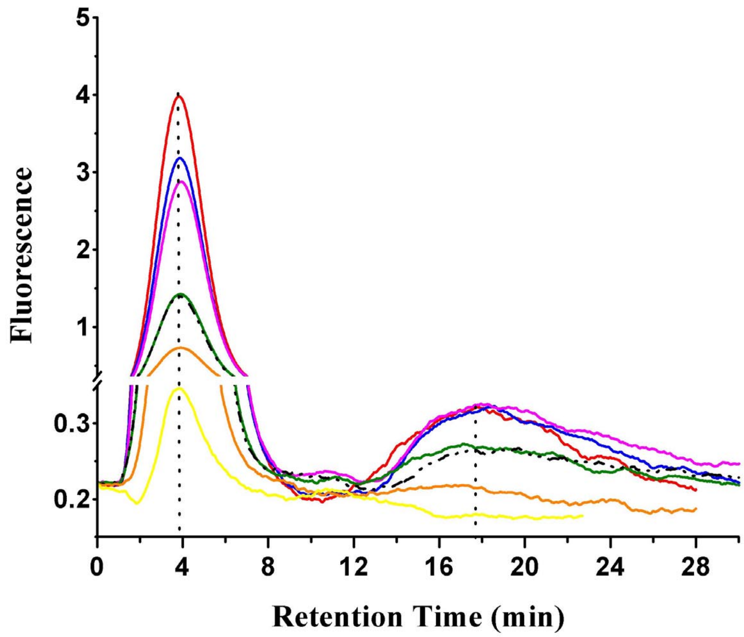

Figure X: 4F analysis of samples through a fresh to marine transition zone, Caloosahatchee River, November 1999

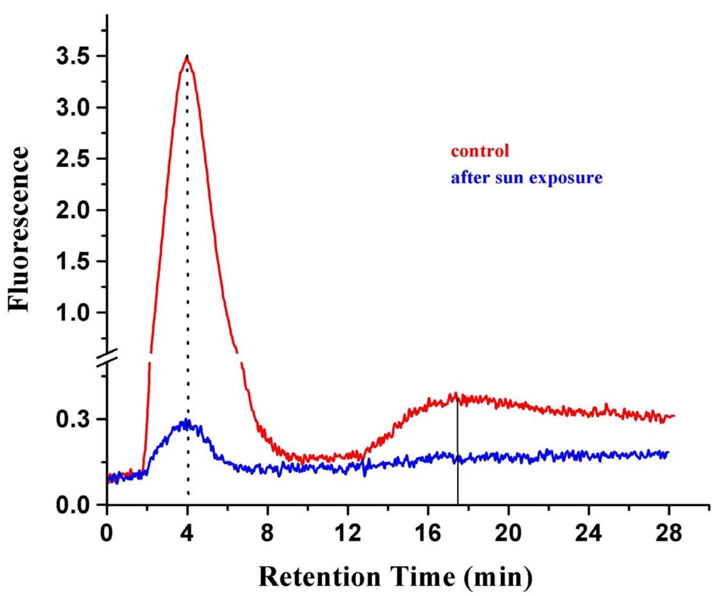

Figure Y: Photodegradation of River CDOM, Caloosahatchee River. 7 days of sunlight exposure

REFERENCES

Beckett, R., Bigelow, J.C., Jue, Z., and Giddings, J.C., 1989, Analysis of Humic Substances Using Field Flow Fractionation. In Aquatic Humic Substance: Influences on Fate and Treatment of Pollutants, eds. J.H. Suffet and P. MaCarthy, ACS Symposium Series 219, American Chemical Society, Washington D.C.

Zanardi E., C. Moore, C.D. Clark, J. Jimenez, G. Jones and R.G. Zika, "Fluorescence Lifetimes of Size-fractionated CDOM in a South Florida Riverine to Marine Transition Zone", ASLO Meeting, Santa Fe, February 1999.

PUBLICATIONS

Clark, C.D. and Rod G. Zika (2000), "Marine Organic Photochemistry: From the Sea Surface to Marine Aerosols". In Handbook of Environmental Chemistry: Marine Chemistry. Ed. P. Wangersky. Springer, Heidelberg. pp 1-23.

Riemer, Daniel D., Peter J. Milne, Rod G. Zika, Willer H. Pos. (2000) Photoproduction of nonmethane hydrocarbons (NMHCs) in seawater." Marine Chemistry 71:177-198.

Clark, C.D., J. Jiminez, E. Zanardi, R. Zika and G. Jones II (1999), "Fluorescence Lifetimes of Dissolved Organic Matter in a Riverine to Marine Transition Zone", Mar. Chem., submitted.

Zanardi-Lamardo, E., Clark, C.D. and Zika, R.G. (2000), "Frit Inlet/Frit Outlet Flow Field Flow Fractionation (4F): Methodology for Colored Dissolved Organic Material (CDOM) in Natural Waters", Anal. Chem. Acta, submitted.